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Kinematical studies of the glass transition in glassy $Se_{80-x}Te_{20}Sb_x$*

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The present paper reports kinematic studies of the glass transition in glassy $Se_{80-x}Te_{20}Sb_x$ alloys using the differential scanning calorimetric technique. The glass transition temperature (T_g) is found to increase monotonically with the heating rate. T_g also increases with the increase of Sb concentration in ternary $Se_{80-x}Te_{20}Sb_x$ system. From the heating rate dependence of glass transition temperature, the activation energy (ΔE_t) for the relaxation time controlling the structural enthalpy, is calculated. The composition dependence of T_g and ΔE_t is discussed in terms of the structure of the Se-Te-Sb glassy system. © *2000 Kluwer Academic Publishers*

1. Introduction

Chalcogenide glasses have attracted a great deal of attention because of their technical importance in various solid state devices. It is well known [1–4] that thermal relaxation occurs in a glassy substance following an instantaneous change in temperature (during the quenching process), as it relaxes from a state of higher enthalpy towards an metastable equilibrium state of lower enthalpy. This type of thermal relaxation depends upon the annealing temperature and may be quite fast near the glass transition temperature. The glass transition is exhibited in Differential Thermal Analyser (DTA) or Differential Scanning Calorimetry (DSC) traces as an endothermic peak or a shift in the base line due to a change in specific heat. However, in chalcogenide glasses, such an endothermic peak can also be observed due to a fast change in enthalpy when the glassy system relaxes quickly due to a decrease in viscosity at the glass transition temperature. DTA or DSC techniques can, therefore, be quite useful in the study of thermal relaxation in glasses.

Among chalcogenide glasses, Se-Te alloys have gained much importance because of their higher photosensitivity, greater hardness, higher crystallization temperature, and smaller aging effects as compared to pure Se glass. The effect of incorporation of Sb on the electrical properties of these alloys has been studied by various workers [5–10]. In general, it is observed that the dc conductivity increases, the activation energy for dc conduction decreases, the thermoelectric power decreases, and the photoconductive decay becomes slower on incorporation of Sb to the binary $Se_{80}Te_{20}$ alloy. To explain the above results it is generally assumed that the addition of Sb in the Se-Te system leads to a cross-linking of Se-Te chains which enhances the disorder in the system and hence leads to a deeper penetration of the localized state into the energy gap.

The present paper reports the kinematic studies of glass transition in $Se_{80-x}Te_{20}Sb_x$ alloys using DSC technique with a view to understand the thermal relaxation phenomena in these glasses. From the heating rate dependence of glass transition temperature, the activation energy of molecular motions and rearrangement near glass transition temperature T_g is calculated and its composition dependence is discussed in terms of the structure of $Se_{80-x}Te_{20}Sb_x$.

2. Experimental

Glassy alloys of $Se_{80-x}Te_{20}Sb_x$ where $x = 0, 5, 10, 15$ have been prepared by a quenching technique. High purity materials (5N pure) Se, Te and Sb in appropriate atomic percent were weighed and sealed in quartz ampoules (Length = 5 cm and internal diameter = 8 mm) in a vacuum of 10^{-2} Pascal. The sealed ampoules were kept inside the furnace at 600 °C (The temp. was raised at a rate of 3 to 4 K/min) for 10–12 h and rocked frequently to make the melt homogeneous. The quenching was done in the water. Glasses thus prepared were ground to make a fine powder for DSC studies. In DSC, the sample is heated at constant rate and the changes in heat flow with respect to an empty reference pan were measured. The samples were kept at room temperature (∼300 K) in dark for about one month for the attainment of thermodynamic equilibrium as stressed by Abkowitz [1] in chalcogenide glasses.

DSC 2910 Differential Scanning Calorimeter (T.A. instrument, USA) was used at four different heating rates 5, 10, 15 and 20 °C/min for the above studies.

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3. Results

Figs 1–4 show typical DSC thermograms at different heating rates in glassy alloy $Se_{80-x}Te_{20}Sb_x$ ($x = 0$, 5, 10 and 15). These figures indicate that well defined endothermic peaks are observed at the glass transition temperature (T_g) rather than a shift in the base line. At higher temperatures, a exothermic peak was also observed which represents the crystallization temperature (T_c). It also indicated that T_g and T_c both shift to higher temperatures as the heating rate is increased from 5 to 20 °C/min. The values of T_g at different heating rates for various glassy alloys are noted from the DSC traces, i.e., the temperatures at which endothermic peaks occur. Such values are given in Table I and plotted in Fig. 5. Table I shows that the value of T_g at a particular heating rate increases with the increase of Sb concentration in $Se_{80-x}Te_{20}Sb_x$ ($x = 0$, 5, 10 and 15) glassy system.

The heating rate dependence of the glass transition temperature in chalcogenide glasses is interpreted in terms of thermal relaxation phenomena. In this kinetic interpretation the enthalpy at a particular temperature and time $H(T, t)$ of the glassy system, after an instantaneous isobaric change in temperature, relaxes isothermally towards a new equilibrium value $H_c(T)$. The relaxation equation can be written in the following

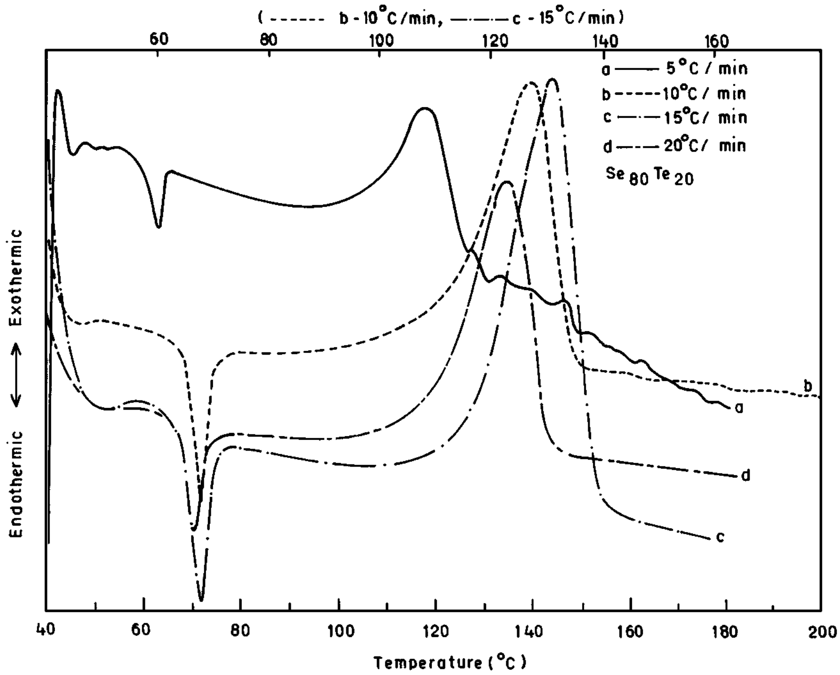

Figure 1 DSC thermograms at different heating rates of $Se_{80}Te_{20}$.

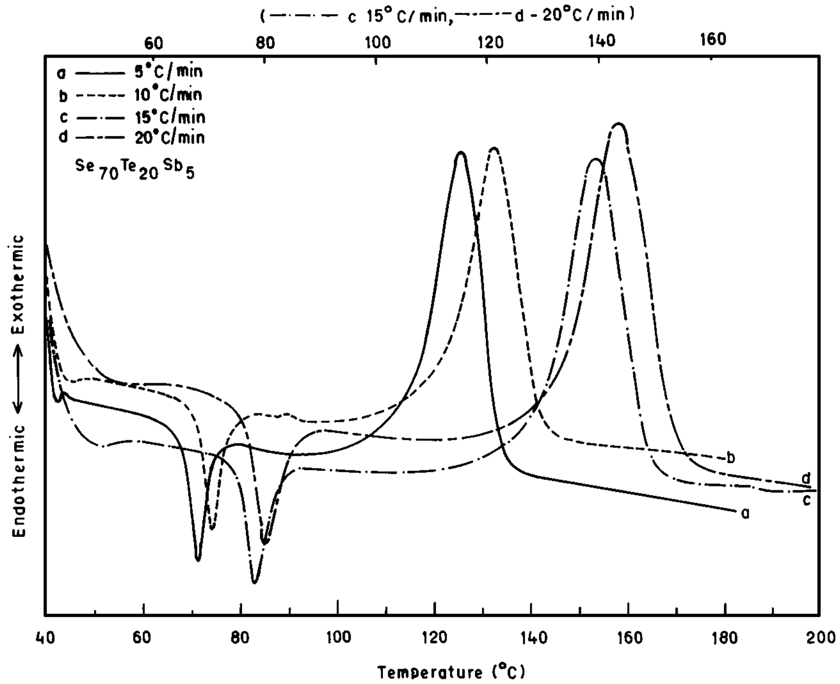

Figure 2 DSC thermograms at different heating rates of $Se_{75}Te_{20}Sb_5$.

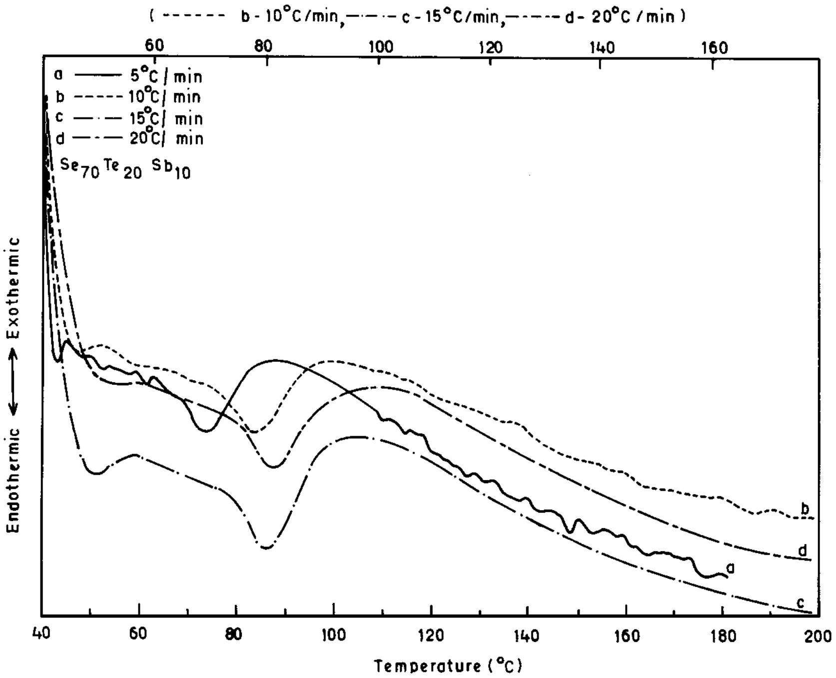

Figure 3 DSC thermograms at different heating rates of $Se_{70}Te_{20}Sb_{10}$.

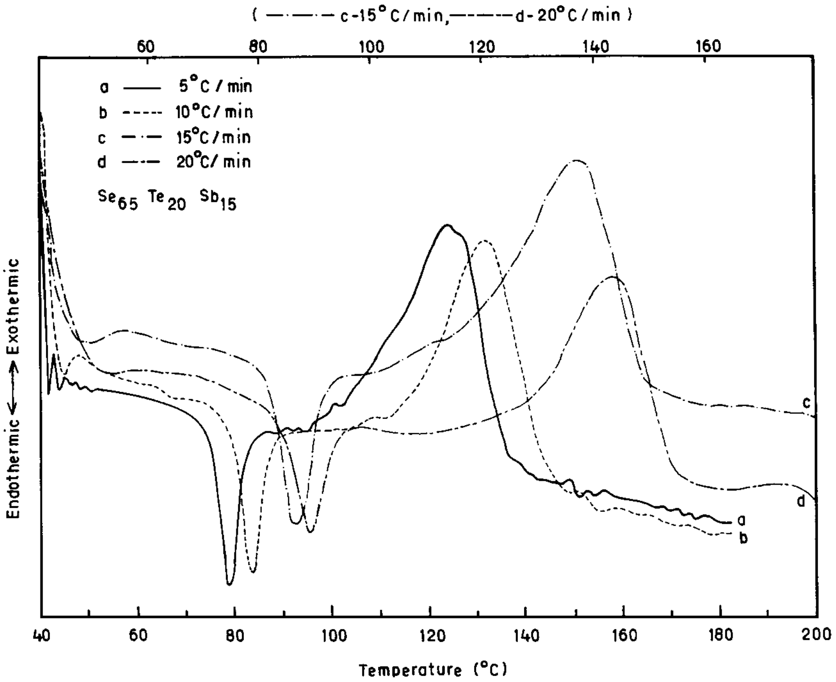

Figure 4 DSC thermograms at different heating rates of $Se_{65}Te_{20}Sb_{15}$.

TABLE I The values of glass transition temperature (T_g) in °C in $Se_{80-x}Te_{20}Sb_x$ ($x = 0$, 5, 10 and 15) at different heating rates

	Heating rates			
Samples	5 °C/min	10 °C/min	15 °C/min	20 °C/min
$Se_{80}Te_{20}$	63.8 °C	68.0 °C	69.3 °C	71.1 °C
$Se_{75}Te_{20}Sb_5$	71.5 °C	74.9 °C	77.3 °C	80.0 °C
$Se_{70}Te_{20}Sb_{10}$	74.6 °C	74.6 °C	80.6 °C	82.0 °C
$Se_{65}Te_{20}Sb_{15}$	79.3 °C	82.1 °C	86.0 °C	88.7 °C

form [5]:

$$\left(\frac{\delta H}{\delta t}\right)_T = -\frac{(H - H_c)}{\tau} \qquad (1)$$

where τ is a temperature dependent structural relaxation time and is given by the following relation

$$\tau = \tau_0 \exp\left(\frac{-\Delta E_t}{RT}\right) \exp[-c(H - H_c)] \qquad (2)$$

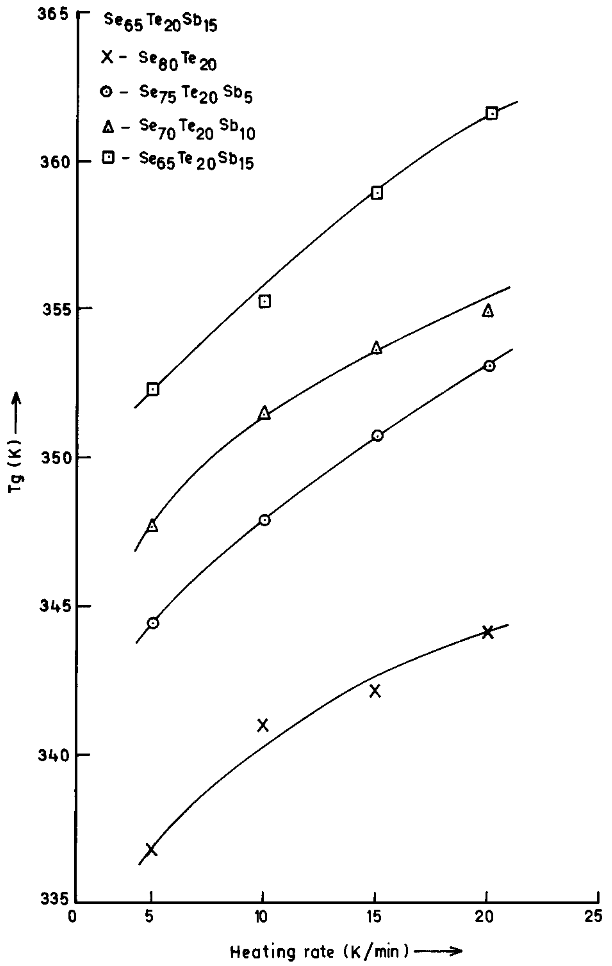

Figure 5 Variation of glass transition temperature (T_g) with heating rates (β) in $Se_{80-x}Te_{20}Sb_x$ ($x = 0, 5, 10$ and 15).

where τ_0 and c are constants and ΔE_t is the activation energy of relaxation time. Using the above equations, it can be shown that

$$\frac{d \ln \beta}{d\left(\frac{1}{T_g}\right)} = \frac{-\Delta E_t}{R} \tag{3}$$

Equation 3 states that $\ln \beta$ vs. $1/T_g$ plot should be straight line and the activation energy envolved in the molecular motions and rearrangements around T_g can be calculated from the slope of this plot.

Fig. 6 shows $\ln \beta$ vs. $1000/T_g$ curves for various glassy alloys in $Se_{80-x}Te_{20}Sb_x$ system. In the present case such plots are straight lines and the values of ΔE_t are calculated from the slopes of the curves shown in Fig. 6.

The results of these calculations are given in Table II. These results show that ΔE_t first decreases and then increases with an increase of Sb concentration (See Fig. 7).

4. Discussion

The glass transition temperature (T_g) of chalcogenide glasses shows coordination number dependence [11] which in turn depends on the percentage of the substituent atom [12]. The glass transition temperature of the system $Se_{80-x}Te_{20}Sb_x$ ($x = 0, 5, 10$ and 15) increases linearly with increasing Sb concentration as shown in Fig. 8 and follows a relation:

TABLE II Composition dependence of the activation energy of relaxation time ΔE_t

Sample	ΔE_t in KJ/mol
$Se_{80}Te_{20}$	174
$Se_{75}Te_{20}Sb_5$	133
$Se_{70}Te_{20}Sb_{10}$	167
$Se_{65}Te_{20}Sb_{15}$	208

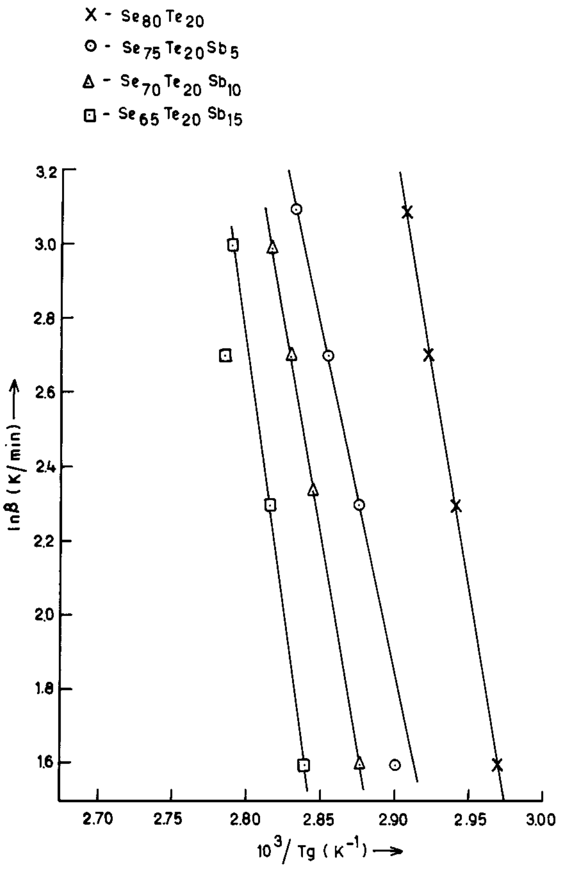

Figure 6 Heating rate dependence of glass transition temperature by a plot of $\ln \beta$ vs. $10^3/T_g$.

$$\ln T_g = aZ + b \tag{4}$$

where Z denotes the average coordination number [13] per atom (calculated in terms of covalent bonding). Equation 4 is similar to the empirical relation proposed by Tanaka [14]. The constant 'a' is positive showing the increase of T_g with Z. The atomic percentage of Sb atom has also been marked in Fig. 8. The results obtained from Fig. 8 are quite consistent with the experimental data.

The increasing trend of T_g with increasing Sb impurity in our system may be explained by considering the structural change due to the introduction of Sb atoms. Glassy Se shows both chain and ring structures [15].

An introduction of Te decreases the Se ring concentration favouring Se-Te mixed rings. A slight increase in polymeric chain of Se is also observed. Sb which

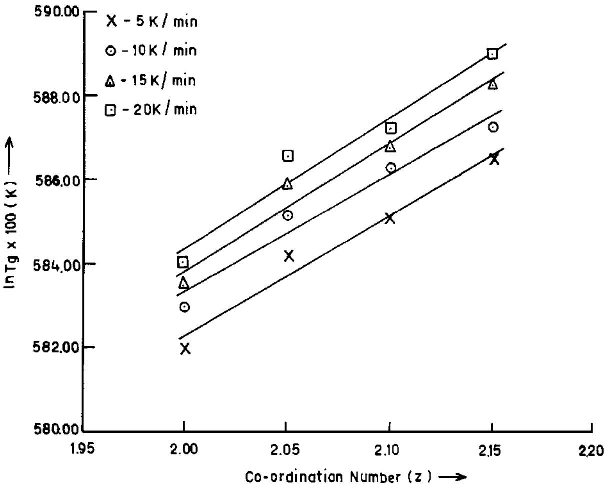

Figure 7 Composition dependence of the activation energy for thermal relaxation (ΔE_t).

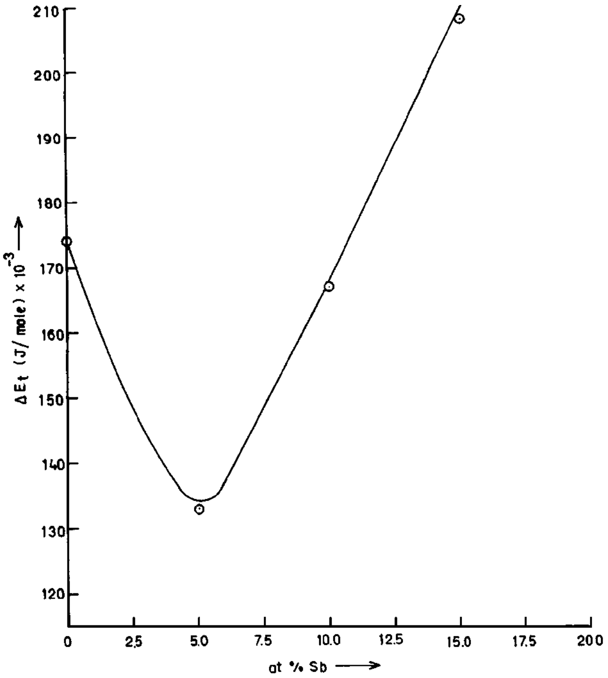

Figure 8 Variation of glass transition temperature (T_g) with average coordination number (Z).

belongs to group V of periodic table when added to the above system may break the Se-Te chains or Se-Te mixed rings to satisfy its coordination number and form a cross linked structure. The addition of Sb also causes a decrease of Se_8 rings and increase chain length [15–17]. Hence T_g increases with increasing Sb concentration.

5. Conclusion

Glass transition temperature has been determined from DSC scans at different heating rates in four glassy samples in $Se_{80-x}Te_{20}Sb_x$ system. In all the glassy alloys, T_g increases monotonically with the increase of heating rate. The activation energy [ΔE_t] of molecular motions and rearrangements around glass transition temperature is determined from the heating rate dependence of T_g. ΔE_t is found to be composition dependent. T_g also increases on the addition of Sb to binary $Se_{80}Te_{20}$ alloy. A correlation of T_g with the increase in coordination number is established. The increase in T_g is explained in terms of the cross-linked structure in Se-Te-Sb system [15].

References

1. M. A. ABKOWITZ in "The Physics of Se and Te," edited by E. Gerlach and P. Grosse (Springer, Berlin, 1979) p. 178.
2. G. C. DAS, M. B. BEVER and D. R. UHIMANN, *J. Non-Cryst. Solids* **1** (1992) 251.
3. M. MATSURRA and K. SUZUKI, *J. Mater. Sci.* **14** (1979) 395.
4. J. P. LARMAGNAC, J. GRENET and P. MICHON, *J. Non-Cryst. Solids* **45** (1981) 157.
5. S. O. KASAP and C. JUHASZ, *J. Mater. Sci.* **21** (1986) 1329.
6. S. K. TRIPATHI and A. KUMAR, *J. Elect. Mater.* **17** (1988) 45.
7. R. ARORA and A. KUMAR, *Phys. Stat. Sol. A* **114** (1989) 833.
8. A. H. ABOUELELA, M. K. EL-MOUSLY and K. S. ABDU, *J. Mater. Sci.* **15** (1980) 871.
9. C. T. MOYNIHAN, A. J. EASTEAL, J. WILDER and J. TUCKER, *J. Phys. Chem.* **78** (1974) 2673.
10. P. AGARWAL, S. GOEL, J. S. P. RAI and A. KUMAR, *Phys. Stat. Sol. A* **127** (1991) 363.
11. C. H. SEEGER and R. K. QUINN, *J. Non-Cryst. Solids* **17** (1975) 286.
12. K. TANAKA, *Phys. Rev.* **B-39** (1989) 1270.
13. R. RANESAN, A. SRINIVASAN and E. S. R. GOPAL, *Proc. Solid State* **35C** (1982) 215.
14. H. FRITZSCHE "Fundamental Phys. of Amorphous Semiconductors" (Springer-Verlag, Berlin, 1981).
15. J. SCHOTTMILLER, M. TABAK, G. LUCOVSKY and A. WARD, *J. Non-Cryst. Solids* **4** (1970) 80.
16. A. EISENBERG, *Polym. Lett.* **1** (1963) 177.
17. K. NAKAYAMA, K. KOJIMA, I. TAMARU, Y. MASAKI, A. KITAGAWA, M. SUZUKI, *J. Non-Cryst. Solids* **198–200** (1996) 758–761.

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